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R. E. HARTLE
J. J. GILVARRY

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ASYMPTOTIC RELATIONS BETWEEN THE THOMAS-FERMI-DIRAC AND THOMAS-FERMI ATOM MODELS. II. EXTENSION OF THE CASE OF LOW ATOMIC NUMBER

R. E. Hartle
Laboratory for Space Sciences,
National Aeronautics and Space Administration,
Goddard Space Flight Center
Greenbelt, Maryland

and

J. J. Gilvarry*
Theoretical Studies Branch, Space Sciences Division,
Ames Research Center,
National Aeronautics and Space Administration,
Moffett Field, California

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*Present address: The Rand Corporation, Santa Monica, California

Goddard Space Flight Center
Greenbelt, Maryland

ABSTRACT

The asymptotic relation between the pressure with exchange in the Thomas-Fermi-Dirac atom model and the corresponding pressure without exchange on the Thomas-Fermi model for the case of low atomic number considered in the first paper of this series is generalized by including a correction corresponding to the first-order Coulomb contribution to the energy of the atom, rather than the kinetic energy of the electrons alone. All terms yielded by the asymptotic solution of March for the Thomas-Fermi-Dirac equation in the limit of small atom radius are included, and the extension of results on the basis of the general asymptotic solution of Rijnierse in this limit is indicated. The expression for the radius of an isolated Thomas-Fermi-Dirac atom for low atomic number obtained previously is extended to include a term corresponding to the Coulomb correction of first order, and compared with a similar result of Jensen. Asymptotic relations between thermodynamic functions (the energy, the compressibility, and parameters associated with the energy and equation of state) on the two models for low atomic number as given previously are extended similarly. Comparison of the extended asymptotic relations between the pressures on the two models is made with numerical results obtained by direct solution of the Thomas-Fermi-Dirac equation.

I. INTRODUCTION

An asymptotic relation expressing the pressure with exchange on on the Thomas-Fermi-Dirac atom model as a function of the corresponding pressure without exchange on the Thomas-Fermi model was obtained by Gilvarry[1] on the basis of the method of March[2] for solving the corresponding differential equations of the models for an infinitesimal atom. In a preceeding paper by Gilvarry, Hartle, and March,[3] hereafter referred to as I, it was shown that the result of Gilvarry follows by a direct physical argument, without the necessity of recourse to solution of differential equations. This possibility arises because the relation between the pressures correspnds to the limiting situation at small volume, where only the kinetic energy of the electrons distributed uniformly throughout the atom need be taken into account (whether for high pressure or for vanishing atomic number).

It was pointed out in I that the physical method presented there could no be used to generalize the results of Gilvarry. The purpose of this paper is to obtain the generalization of these results by taking into account all the terms in the asymptotic solution of the Thomas-Fermi-Dirac equation for small atom radius which can be determined by the method of March. Physically, this procedure corresponds to considering in the relation between the pressures with and without exchange the effect of the Coulomb interactions to first order as well as the effect of the kinetic energy of the electrons. In addition, the expression obtained in I for the radius of a Thomas-Fermi-Dirac atom in the limit

of vanishing atomic number will be correspondingly generalized, and the connection with prior results of Jensen[4] will be discussed. Results for thermodynamic parameters as generalized in the case of low atomic number also will be considered.

Only a restricted number of terms in the solution of the Thomas-Fermi-Dirac equation for the limit of vanishing atom radius can be obtained by the method of March, because of the appearance of divergences. In particular, only terms through quadratic in the exchange parameter can be found. However, Rijnierse[5] has developed a method of obtaining systematically any desired number of terms (and of arbitrary order in the exchange parameter) in the solution of the Thomas-Fermi-Dirac equation for the case of small atom radius. The extension of results on the basis of the general solution by Rijnierse will be indicated.

The treatment is restricted to the case of zero absolute temperature throughout. The atom is considered spherically symmetric.

II. ASYMPTOTIC RELATIONS

The Thomas-Fermi-Dirac equation[6] is

$$d^2\psi/dx^2 = x[(\psi/x)^{1/2} + \epsilon]^3, \tag{1}$$

where ϵ is the exchange parameter $(3/32\pi^2)^{1/3} Z^{-2/3}$ for an atom of atomic number Z, and x is a dimensionless variable connected with the

radial distance r in the atom by $r = \mu x$, in which μ is the scale length $(9\pi^2/128Z)^{1/3}$ in atomic units. The Thomas-Fermi-Dirac function $\psi(x)$ for a neutral atom satisfies the initial and boundary conditions

$$\psi(0) = 1, \qquad [d\psi/dx]_{x=x_b} = \psi_b/x_b, \tag{2a, b}$$

respectively, where ψ_b is the boundary value of ψ corresponding to the radius x_b of the atom. When ϵ vanishes, Eq. (1) reduces to the Thomas-Fermi equation $d^2\phi/dx^2 = \phi^{3/2}/x^{1/2}$, where the Thomas-Fermi function ϕ is subject to initial and boundary conditions exactly analogous to those of Eqs. (2).

Asymptotic solutions for the Thomas-Fermi-Dirac function in the case of small atom radius have been obtained by March and Gilvarry by means of a method introduced by the former. The procedure consists in expanding ψ in a Taylor series about the atom boundary, imposing the initial and boundary conditions, and obtaining systematically the partial sums ψ_n of degree $n = 1, 3, 5, \cdots$ in $x - x_b$. The first three partial sums are given recursively by

$$\psi_1 = 3^{2/3}(x/x_b^2) - 2\cdot 3^{1/3}(x/x_b)\epsilon + x\epsilon^2 \tag{3a}$$

$$\psi_3 = \psi_1 + 1 - \frac{3}{2}(x/x_b) + \frac{1}{2}(x/x_b)^3 \tag{3b}$$

$$\psi_5 = \psi_3 - (3/10)\, x/x_b. \tag{3c}$$

These results are valid in the limit of vanishing atom radius x_b .

It was shown by Gilvarry and in I that the Thomas-Fermi-Dirac function corresponding to the limit of a uniform distribution of electrons confined to the atom volume is the partial sum ψ_1 of Eq. (3a) and must include terms linear and quadratic in ϵ . Of the three terms, the initial one arising from the chemical potential of an electron is the dominant one and the last two correspond to the effect of exchange. The first term dependent on ϵ was obtained by March and the second by Gilvarry. The original results of Gilvarry and those of I follow from the boundary value $\psi_{1,b}$ of ψ_1 , upon which the pressure depends. This partial sum corresponds to the effect of the kinetic energy of the electrons only.

The second partial sum ψ_3 of Eq. (3b) differs from ψ_1 by the last three terms, which represent the effect of the variation of the potential in the atom computed on the assumption that the electron density is uniform. These terms were obtained first by Gilvarry, by means of a physical argument. However, one notes that the three terms cancel for $x = x_b$, and hence the boundary values $\psi_{1,b}$ and $\psi_{3,b}$ corresponding to the first two partial sums are equal. It follows that the associated pressures agree and hence the effect on the Thomas-Fermi-Dirac function of the variation of the potential implied by a uniform electron distribution does not change the results of I inferred by considering the effect of the kinetic energy alone. This fact was noted by Gilvarry.

The partial sum ψ_5 differs from ψ_3 by a term $-(3/10)\ x/x_b$ which arises from the contribution of the electrostatic electron-nucleus and electron-electron interactions in addition to the kinetic energy, producing nonuniformity of the electron distribution in the atom. Since this correction to ψ_3 does not vanish at the atom boundary, the corresponding boundary value $\psi_{5,b}$ does not equal $\psi_{3,b}$ and the associated pressures differ. The object of this paper is to obtain the modification to the results of I arising from inclusion in the Thomas-Fermi-Dirac function of the effect of the term in question, arising from the electrostatic interaction when the electron distribution is not uniform. This term representing the Coulomb correction on the boundary value of the Thomas-Fermi-Dirac function was obtained first by March.

Note that Eq. (3c) for ψ_5 contains all terms in ψ which can be determined by the method of March. Terms of higher order are given by Rijnierse.

In what follows, it is necessary to consider only the boundary value

$$\psi_b = 3^{2/3}/x_b - 2\cdot 3^{1/3}\,\epsilon + x_b\epsilon^2 - 3/10\,, \tag{4}$$

corresponding to ψ_5, since the pressure depends only upon boundary values. In this expression, the first three terms correspond to the results of Gilvarry and in I; the last term arises from the Coulomb correction and yields the extension of the results of I obtained in this paper.

The pressure p_{ex} with exchange corresponding to a Thomas-Fermi-Dirac atom at zero temperature is given by

$$p_{ex} = \frac{Z^2 e^2}{10\pi\mu^4}\left\{\left[\left(\frac{\psi_b}{x_b}\right)^{1/2} + \epsilon\right]^5 - \frac{5}{4}\epsilon\left[\left(\frac{\psi_b}{x_b}\right)^{1/2} + \epsilon\right]^4\right\}, \tag{5}$$

where e is the electronic charge. When ϵ vanishes, this expression reduces to the corresponding pressure p of a Thomas-Fermi atom given by

$$p = (Z^2 e^2/10\pi\mu^4)\ (\phi_b/x_b)^{5/2} \tag{6}$$

in terms of ϕ_b, the value of ϕ at the atom boundary. Upon substituting Eq. (4) into Eq. (5) and retaining terms of significant order, one obtains

$$p_{ex} = p_0\ [1 - 5\epsilon x_b/4\cdot 3^{1/3} - 3^{1/3}x_b/4], \tag{7}$$

where p_0 is the Thomas-Fermi pressure in the limit $x_b \to 0$, given by[6]

$$p_0 = (2^8/15\pi^3)(2/\pi^2)^{1/3}\ (e^2/a_0^4)\ Z^{10/3}\ x_b^{-5} \tag{8}$$

in terms of the radius a_0 of the first Bohr orbit for hydrogen.

The expression for the pressure p_{ex} of Eq. (7) was obtained by March[2] from a form for ψ_b corresponding to Eq. (4) with the exception that the quadratic term in ϵ was ommited; Gilvarry pointed out that

March's result for p_{ex} is valid through terms in ϵ higher than were included explicitly. The leading term p_0 of Eq. (7) is just the contribution to the pressure from the kinetic energy of a uniform distribution of Z electrons in the atom volume. The second term is simply the exchange correction to such a gas of free electrons. The last term can be identified as the sum of the pressure contributions p_{en} and p_{ee} from the electron-nucleus and electron-electron interactions, respectively, calculated on the assumption of a uniform distribution of electrons.

It follows from Eq. (7) that the Thomas-Fermi-Dirac pressure p_{ex} can be expressed as a function of the limiting form p_0 of Eq. (8) for the Thomas-Fermi pressure by the asymptotic relation

$$p_{ex} = p_0 \left[1-(1+3^{2/3}\epsilon^{-1}/5)(\mathcal{P}_0/p_0)^{1/5}\right] \tag{9}$$

in terms of the constant pressure $\mathcal{P}_0$ (independent of Z) given by

$$\mathcal{P}_0 = [5^4/(3\cdot 2^{10}\pi^7)]\, e^2/a_0^4, \tag{10}$$

as was noted by Gilvarry. The fact that the Thomas-Fermi-Dirac pressure p_{ex} of Eq. (9) includes the effects to first order of the electron-nucleus and electron-electron interactions raises the possibility that p_{ex} can be expressed as a function of the corresponding Thomas-Fermi pressure which includes the effects of these interactions. One obtains the latter pressure including such interactions to first order by equating ϵ to zero in Eq. (7) to yield

$$p_M = p_0 (1 - 3^{1/3} x_b/4) , \tag{11}$$

where p_M is the pressure derived by March.[2] Factoring $(1 - 3^{1/3} x_b/4)$ from the expression in square brackets of Eq. (7), one obtains

$$p_{ex} = p_M [1 - (5\epsilon x_b/4 \cdot 3^{1/3}) (1 + 3^{1/3} x_b/4)] , \tag{12}$$

which differs from Eq. (7) in that p_0 is replaced by p_M, which contains the Coulomb correction.

The terms neglected in the square brackets of Eq. (7) are of form $O(x_b^2)$. The perturbation analysis of March leading to this equation cannot yield the coefficient of the term $O(x_b^2)$; however, this coefficient can be determined by consideration of the general form of the Thomas-Fermi-Dirac energy u_{ex}. The energy to which Eq. (7) corresponds is[1]

$$u_{ex} = u_0 [1 - (5\epsilon x_b/2 \cdot 3^{1/3}) - 3^{1/3} x_b/2] \tag{13}$$

where u_0 is the Thomas-Fermi energy associated with p_0. One can infer from this expression and the results of Rijnierse that the general asymptotic form of u_{ex} for the case of small x_b must be

$$u_{ex} = u_0 \sum_{n=0}^{\infty} b_n x_b^n \tag{14}$$

with the coefficients b_n dependent on ϵ in general. Since u_0 varies as x_b^{-2}, the corresponding pressure is

$$p_{ex} = p_0 \sum_{n=0}^{\infty} \left(\frac{2-n}{2}\right) b_n x_b^n \tag{15}$$

and one notes the complete absence of a term of form $p_0\, O(x_b^2)$, since the corresponding coefficient vanishes when $n = 2$. This conclusion is consonant with the general solution of Rijnierse for p_{ex} given by Eq. (A1) in the Appendix.

One notes that the factoring operation leading to Eq. (12) introduced a term of order ϵx_b^2 into the expression in square brackets. It follows from the preceding argument that the corresponding coefficient is exact, since the form of p_{ex} preceding the factoring operation contained no such term. This fact is important in what follows, since it will be demanded that the final asymptotic relation for p_{ex} vanish when the radius x_b of the atom has the value $x_{b,Z}$ corresponding to the isolated Thomas-Fermi-Dirac atom. Terms of order ϵx_b^2 must be retained in the asymptotic expression for p_{ex}, since they are of the same order as $x_{b,Z}$ when x_b has the value $x_{b,Z}$ corresponding to the isolated atom, as will appear.

Equation (12) can be put in the form

$$p_{ex} = p_M \left[1 - (5\epsilon x_b/4\cdot 3^{1/3})\ (1 + 3^{1/3} x_b/20) - \epsilon x_b^2/4\right] \tag{16}$$

by adding and subtracting $p_M \epsilon x_b^2/16$. In the limit of small x_b at a fixed value of Z, the Thomas-Fermi pressure p approaches asymptotically the values of p_M and p_0. However, for small x_b, in general, p_M should be a better approximation to p than is p_0. Hence, for the limit in question, Eq. (16) can be written with suppression of the subscript M on p as

$$p_{ex} = p\,[1-(\wp_0/p)^{1/5} - Z^{2/3}\,(\wp_1/p)^{2/5}] \tag{17}$$

by substitution for ϵ and elimination of x_b with use of Eq. (11). The constant pressure $\wp_1$ is given by

$$\wp_1 = (4/5)^5\,(3\pi^2/2)^{5/6}\,\wp_0\,, \tag{18}$$

in terms of $\wp_0$ of Eq. (10).

Equation (17) represents the proper asymptotic relation between the Thomas-Fermi-Dirac pressure p_{ex} and the Thomas-Fermi pressure p when the effects on the pressures of not only the kinetic energy of the electrons but also their Coulomb interaction to first order are taken into account. On the same basis as in the argument of Gilvarry and as given in I, the result holds in the first instance for infinitesimal volume and should be valid in the two limits corresponding to infinite pressure for arbitrary atomic number and to vanishing atomic number for arbitrary pressure. In general, Eq. (17) should hold for a range of atomic number at low Z, rather than simply in the asymptotic limit $Z \to 0$.

One notes from Eq. (17) that one obtains $p_{ex} = p$ in the limit $p \to \infty$ at constant Z, where the contributions from the exchange and Coulomb energies vanish. In contrast to the limit $x_b \to 0$ at fixed Z corresponding to $p \to \infty$, consider the limit $Z \to 0$ at a fixed value of the Thomas-Fermi pressure p. For this case, the asymptotic expression of Eq. (8) implies $x_b \to 0$ as $Z \to 0$, independently of pressure p. The last term in Eq. (17) representing a contribution from the Coulomb energy vanishes for the limit in question and the resulting expression

$$p_{ex} = p\,[1-(\wp_0/p)^{1/5}] \tag{19}$$

is that obtained by Gilvarry and in I.

Further generalization of the asymptotic relation of p_{ex} to p is carried out in the Appendix by using the general expression for p_{ex} obtained by Rijnierse. In this instance, for sufficiently small x_b, Eq. (A5) can be written as

$$p_{ex} = p\,[1-(\wp_0/p)^{1/5} - Z^{2/3}\,(\wp_1/p)^{2/5} - Z^{4/3}\,(\wp_2/p)^{3/5}] \tag{20}$$

in terms of the constant pressure

$$\wp_2 = [(2/5)^4\,(18\pi^4)^{1/3}/7]^{5/3}\,\wp_0 \tag{21}$$

This procedure yields a result that should be valid over wider ranges of pressure than the corresponding Eq. (17). One notes, of course, that the same asymptotic results follow from either Eq. (17) or Eq. (20) when one takes the limits $p \to \infty$ at fixed Z or $Z \to 0$ at fixed p.

A maximum atom radious $x_{b,Z}$ for any value of Z corresponds to the isolated Thomas-Fermi-Dirac atom with zero pressure on its boundary. The boundary value $\psi_{b,z}$ of ψ_b in the case $p_{ex} = 0$ must satisfy the Jensen boundary condition

$$\psi_{b,z}{}' / x_{b,z} = (\epsilon/4)^2 , \tag{22}$$

which constrains $x_{b,z}$ to be a function of Z. The Jensen condition conjoined with ψ_b of Eq. (4) yields a quadratic equation for $x_{b,z}$ with a corresponding ambiguous sign in the root. Eq. (17) requires $p > \wp_0$ and since $p(x_b)$ is a monotone-decreasing function,[7] the minumum root must be taken. Hence, the radius $x_{b,z}$ of the Thomas-Fermi-Dirac atom on the basis of Eq. (4) is

$$x_{b,z} = \frac{4}{5} 3^{1/3} \epsilon^{-1} \left(1 - \frac{1}{5} 3^{2/3} \epsilon^{-1}\right) \tag{23}$$

or, equivalently,

$$x_{b,z} = \frac{4}{5} (32\pi^2)^{1/3} Z^{2/3} \left[1 - \frac{1}{5} (96\pi^2)^{1/3} Z^{2/3}\right], \tag{24}$$

where terms of significant order have been retained. One verifies directly that $\epsilon x_{b,Z}^2$ and $x_{b,Z}$ are of the same order, as stated previously.

Direct substitution of the result of Eq. (24) into p_{ex} of Eq. (17) yields

$$p_{ex}(x_{b,Z}) = 0 \tag{25}$$

to the order of terms considered. Thus, Eq. (24) represents the radius of an isolated Thomas-Fermi-Dirac atom as a function of atomic number in the limit $Z \to 0$, in conformity with the assumption that x_b be small. The leading term of Eq. (24), obtained in I, corresponds to the effect produced by the exchange force which tends to contract the electron cloud (through its effect on the electrostatic potential energy). The second term corresponds to a contribution from the Coulomb interaction, in conformity with the fact that the total electrostatic attraction of the nucleus on the electrons is greater than the repulsion of the electrons on themselves. To the isolated Thomas-Fermi-Dirac atom with radius $x_{b,Z}$ given by Eq. (24) and meeting Eq. (25), a compressed Thomas-Fermi atom of the same radius exists for which the pressure p satisfies

$$p(x_{b,Z}) = \wp_0 \left[1 + (16/5)\,(3\pi^2/2)^{1/3}\, Z^{2/3}\right]. \tag{26}$$

This expression generalizes a result of I to low atomic number, since it yields the physical interpretation of $\wp_0$ given by $p(x_{b,Z}) = \wp_0$ in the limit $Z \to 0$. Notice that as Z increases, the pressure at the boundary of the isolated Thomas-Fermi-Dirac atom remains zero, but that for the associated Thomas-Fermi atom of the same radius becomes larger with Z.

A difficulty arises when one seeks the next correction term to $x_{b,Z}$ of Eq. (24) from Rijnierse's general solution for p_{ex} given by Eq. (A1) in the Appendix. In this case, $x_{b,Z}$ is fixed by Eq. (25). However, a subseries in the square brackets of Eq. (A1) exists whose i-th term varies as $\epsilon^i x_b^{i+2}$ and consequently as $x_{b,Z}^2$ at the isolated atom boundary. It is unfortunate that these terms contribute to the next correction to $x_{b,Z}$ because, in principle, one must sum an infinite series to obtain the corresponding coefficient. In fact, the first few terms of this subseries indicate at best a very slow rate of convergence.

Jensen[4] has determined the equilibrium atom radius of a spherically symmetric and uniform distribution of electrons in the field of a nucleus by minimizing the Hamiltonian

$$H = \mathcal{K}_k \int \rho^{5/3} d\tau - e \int V_n \rho d\tau + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d\tau d\tau' - \mathcal{K}_A \int \rho^{4/3} d\tau, \qquad (27)$$

where ρ is the electron density, V_n is the nuclear potential and the constants are given by $\mathcal{K}_k = (3/10)(3/\pi)^{2/3}\pi^2 e^2 a_0$ and $\mathcal{K}_A = (3/4)(3/\pi)^{1/3} e^2$.

The first integral over the atom volume represents the kinetic energy, while the following two are the electron-nucleus and electron-electron potential energies, respectively, and the last integral represents the exchange energy. Mininizing the Hamiltonian with respect to the atom radius for the case of a uniform density $\rho = Z/v$ in terms of the atom volume $v = (4/3)\pi\mu^3 x_b^3$, one obtains

$$x_{b,Z} = \frac{4}{5}(32\pi^2)^{1/3} Z^{2/3} \left[1 + \frac{1}{5}(96\pi^2)^{1/3} Z^{2/3}\right]^{-1}, \qquad (28)$$

which represents the atom radius determined by Jensen. Binomial expansion of this result yields agreement with Eq. (24) through terms of order $Z^{4/3}$.

In deriving Eq. (28), Jensen assumed that the electron distribution is uniform. He did not state any restriction on the atomic number Z. However, it is obvious from the argument of Gilvarry and that presented in I that $Z \to 0$ is the necessary and sufficient condition that the electron distribution in an isolated Thomas-Fermi-Dirac atom be uniform. It follows, in fact, that Eq. (28) is subject to the restriction that the atomic number Z be small, and that the result as expressed by Eq. (24) is no more accurate than the binomial expansion of Eq. (28) which corresponds to it. As a check, one notes that Eq. (28) implies that $x_{b,Z}$ approaches a constant for large Z, which is clearly invalid since $x_{b,Z}$ is know to vary as $Z^{1/3}$ in this limit.[8]

III. THERMODYNAMIC PARAMETERS

For sufficiently small x_b, the total Thomas-Fermi-Dirac energy u_{ex} with exchange, related to the pressure by $p_{ex} = -du_{ex}/dv$ can be derived by integration of Eq. (7). Neglecting the resulting integration constant,[9] one obtains

$$u_{ex} = u_0 \left[1-2(1+3^{2/3}\,\epsilon^{-1}/5)\,(\wp_0/p_0)^{1/5}\right], \tag{29}$$

in terms of the Thomas-Fermi energy u_0 without exchange corresponding to p_0, given by

$$u_0 = (6/5)\,(4/\pi)^{2/3}\,(e^2/a_0)\,Z^{7/3}/x_b^2\,. \tag{30}$$

In analogy with the Thomas-Fermi-Dirac pressure p_{ex} of Eq. (17), the energy u_{ex} can be expressed as a function of the Thomas-Fermi pressure p_M and the corresponding energy u_M given by

$$u_M = u_0 \left[1-\frac{2}{5}\,3^{2/3}\,\epsilon^{-1}\,(\wp_0/p_0)^{1/5}\right] \tag{31}$$

which one obtains by integration of Eq. (11). Accordingly, one has

$$u_{ex} = u_M \left[1-2\,(\wp_0/p_M)^{1/5} - \frac{9}{2}\,Z^{2/3}\,(\wp_1/p_M)^{2/5}\right]. \tag{32}$$

The last term in the square brackets of Eq. (32) is of form ϵx_b^2 and has been retained since it is of the same order as $x_{b,z}$ at the isolated atom radius (as has been pointed out previously). The general solution for u_{ex} obtained by Rijnierse shows the presence of a term of form x_b^2 with coefficient independent of ϵ, which clearly can be ignored. Hence, all terms have been retained in Eq. (32) for u_{ex} which are significant for $x_b = x_{b,z}$ in the case corresponding to the isolated atom, where Eq. (25) holds. Thus the ratio

$$u_{ex}/u = 1 - 2\,(\wp_0/p)^{1/5} - \frac{9}{2} Z^{2/3}\,(\wp_1/p)^{2/5} \qquad (33)$$

represents the asymptotic relation between the Thomas-Fermi-Dirac energy u_{ex} and the Thomas-Fermi energy u when the effects on the energies of not only the kinetic energy of the electrons but also the Coulomb interaction to first order are taken into account. This expression should be valid for an extended range of low atomic number as compared to the corresponding result of I.

The result of Eq. (33) should be valid in the two limits corresponding to infinite pressure for arbitrary atomic number and to vanishing atomic number for arbitrary pressure. For the limit $p \to \infty$ independent of Z, one obtains $u_{ex}/u = 1$; on the other hand, the last term on the right-hand side corresponding to the Coulomb correction vanishes for the limit $Z \to 0$ independently of p, yielding the result of Gilvarry and as given in I.

If one defines the Thomas-Fermi-Dirac parameters $\gamma_{0,ex}$ and $\epsilon_{0,ex}$ with exchange by $u_{ex} = p_{ex} v/(\gamma_{0,ex} - 1)$ and $\epsilon_{0,ex} = -d\ln p_{ex}/d\ln v$, respectively, in analogy with the corresponding definitions $u = pv/(\gamma_0 - 1)$ and $\epsilon_0 = -d\ln p/d\ln v$ for the Thomas-Fermi case without exchange, one can obtain $\gamma_{0,ex}$ and $\epsilon_{0,ex}$ in terms of p_0 for x_b small. The results for $\gamma_{0,ex}$ and $\epsilon_{0,ex}$ can then be expressed in terms of the Thomas-Fermi pressure p_M of March and the corresponding parameters $\gamma_{0,M}$ and $\epsilon_{0,M}$ determined by $u_M = p_M v/(\gamma_{0,M} - 1)$ and $\epsilon_{0,M} = -d\ln p_M/d\ln v$, respectively. Consequently, one has

$$\gamma_{0,ex} = \gamma_0 \left[1 - \frac{8}{5}(\wp_0/p)^{1/5} - \frac{14}{5} Z^{2/3}(\wp_1/p)^{2/5}\right]\left[1 - 2(\wp_0/p)^{1/5} - \frac{9}{2} Z^{2/3}(\wp_1/p)^{2/5}\right]^{-1}, \quad (34a)$$

$$\epsilon_{0,ex} = \epsilon_0 \left[1 - \frac{4}{5}(\wp_0/p)^{1/5} - \frac{3}{5} Z^{2/3}(\wp_1/p)^{2/5}\right]\left[1 - (\wp_0/p)^{1/5} - Z^{2/3}(\wp_1/p)^{2/5}\right]^{-1}, \quad (34b)$$

where $\gamma_{0,M}$, $\epsilon_{0,M}$ and p_M have been replaced by their asymptotic equivalents γ_0, ϵ_0 and p, respectively, for the case of small x_b. Note that γ_0 and ϵ_0 in the present context are given by

$$\gamma_0 = \frac{5}{3}\left[1 + (3^{1/3}/10)\, x_b\right], \quad (35a)$$

$$\epsilon_0 = \frac{5}{3}\left[1 + (3^{1/3}/20)\, x_b\right], \quad (35b)$$

respectively, from the results of March,[2,10] and not simply by the limits $\gamma_0 = \epsilon_0 = 5/3$ appropriate to the discussion of I. Thus, the parameters γ_0 and ϵ_0 are not identical for the case of low Z considered here. These expressions generalize the results of I to an extended range of low atomic number.

The results obtained represent generalizations of the corresponding expressions first obtained by Gilvarry. For the case of vanishing atomic number independent of pressure p one cannot take $p >> \wp_0$, in general, since $\wp_0$ is 0.01982Mb numerically. However, when the pressure is sufficiently high, a binomial expansion of Eq. (34) yields the approximations

$$\gamma_{0,ex} = \gamma_0 \left[1 + \frac{2}{5}(\wp_0/p)^{1/5} + \frac{17}{10} Z^{2/3} (\wp_1/p)^{2/5}\right], \tag{36a}$$

$$\epsilon_{0,ex} = \epsilon_0 \left[1 + \frac{1}{5}(\wp_0/p)^{1/5} + \frac{2}{5} Z^{2/3} (\wp_1/p)^{2/5}\right], \tag{36b}$$

generalizing the original results of Gilvarry. Since the Coulomb correction terms varying as $Z^{2/3}(\wp_1/p)^{2/5}$ in Eqs. (34) and (36) vanish for the limit $Z \to 0$ at constant p, one notes that the results of I obtain in this case.

The Thomas-Fermi-Dirac compressibility $\beta_{0,ex}$ with exchange is defined by $\beta_{0,ex} = - d\ln v / dp_{ex}$ in analogy with the Thomas-Fermi compressibility $\beta_0 = - d\ln v / dp$ without exchange. In terms of the differential parameters $\epsilon_{0,ex}$ and ϵ_0 introduced previously, one has

$$\beta_{0,ex} = (\epsilon_{0,ex}\, p_{ex})^{-1}, \tag{37a}$$

$$\beta_0 = (\epsilon_0\, p)^{-1}, \tag{37b}$$

respectively, by definition. The compressibility $\beta_{0,ex}$ of Eq. (37a) when combined with Eqs. (17), (36b) and (37b) can be expressed as a function of p_M and the corresponding compressibility $\beta_{0,M} = (\epsilon_{0,M}\, p_M)^{-1}$. Accordingly, for sufficiently small x_b, one obtains

$$\beta_{0,ex} = \beta_0 \left[1 - \frac{4}{5}(\wp_0/p)^{1/5} - \frac{3}{5} Z^{2/3} (\wp_1/p)^{2/5}\right]^{-1}, \tag{38}$$

upon replacing p_M and $\beta_{0,M}$ by the corresponding p and β_0, respectively. In this expression, one has

$$\beta_0 = \frac{3}{5} p_0^{-1} \left[1 + (3^{1/3}/5)\, x_b\right], \tag{39}$$

from results of March.[2,10] For the restricted situation where the pressure p is sufficiently high, the compressibility is approximated by

$$\beta_{0,ex} = \beta_0 \left[1 + \frac{4}{5}(\wp_0/p)^{1/5} + \frac{3}{5} Z^{2/3} (\wp_1/p)^{2/5}\right], \tag{40}$$

which generalizes the result of I for the case of low atomic number. Note that, the compressibility reduces to the result of I for the limit $Z \to 0$, independent of p.

The results for thermodynamic parameters obtained in this section can be generalized on the basis of the results of Rijnierse in an obvious manner.

IV. COMPARISON WITH NUMERICAL DATA

The Thomas-Fermi-Dirac pressure p_{ex} as a function of the corresponding Thomas-Fermi pressure p has been plotted by Gilvarry for a number of values of Z from available numerical solutions for these quantities. The solid lines for constant Z in Fig. 1 where constructed from his results. The selection of values of Z includes the practical limits represented by $Z = 92$ and $Z = 2$. The limit line in the figure corresponds to the asymptotic expression of Eq. (19) for the limit $Z \to 0$.

The asymptotic expression of the Thomas-Fermi-Dirac pressure p_{ex} given by Eq. (17), which includes the Coulomb correction to first order, is shown by dashed lines in Fig. 1. One notes that at any value of p, the curves of constant Z approach the limit line as $Z \to 0$, in the family of solid curves corresponding to the exact solutions and in the family of dashed curves corresponding to the asymptotic result of Eq. (17). This fact is more obvious in Fig. 1 for the higher pressures than for the lower. Further, one notes that at sufficiently high pressure, all

curves (solid and dashed) approach the tangent line $p_{ex} = p$ to the limit line. Thus, the march of the curves corresponding to the asymptotic expression of Eq. (17) is consistent with the limit line of Gilvarry and with the exact solutions.

Figure 2 shows values of p_{ex} as a function of p of intermediate magnitude as solid curves on an enlarged scale, from numerical results of Metropolis and Reitz.[11] Corresponding curves from the asymptotic result of Eq. (17) appear dashed. Although the data are limited, it is apparent (most prominently for $Z = 14$) that the asymptotic expression approaches the corresponding exact result for fixed atomic number as the pressure increases. Further, it is clear from the figure that for a given value of Z, there exists a Thomas-Fermi pressure p, say $P(Z)$, such that for $p > P(Z)$ the asymptotic expression p_{ex} of Eq. (17) is a closer approximation to the actual Thomas-Fermi-Dirac pressure than is the limit of Eq. (19) corresponding to $Z \to 0$. For example, $P(14)$ is approximately 35 Mb while $P(92)$ is about 350 Mb. It is obvious that for $p > P(Z)$, Eq. (17) must be a valid approximation to the actual Thomas-Fermi-Dirac pressure for Z in the intermediate and large range rather than merely in the asymptotic limit $Z \to 0$.

The lower range of pressures is covered by Fig. 3, where the solid curves representing exact solutions for p_{ex} vs p at low and fractional values of Z were plotted from results given by Gilvarry. The dashed curves yield the asymptotic results of Eq. (17). It is obvious that in the families of solid and of dashed curves, individually, the value

of the Thomas-Fermi-Dirac pressure approaches that given by the limit line as $Z \to 0$ for fixed p or as $p \to \infty$ for fixed Z. Thus, the results are consistent in this sense with the theory given. Moreover, one notes that the courses of the dashed relative to the solid curves are essentially the same in Fig. 3 as in Fig. 2. Thus, one can infer that Eq. (17) should yield a valid approximation to the true Thomas-Fermi-Dirac pressure for low values of Z when one has $p > P(Z)$. However, the data of Fig. 3 are too limited to specify $P(Z)$ numerically in the limit of low atomic number, although $P(0.04)$ must be of the order of a megabar, as judged by extrapolation from the data.

The salient feature of Fig. 3, however, is that for increasing values of Z at fixed p, the asymptotic values p_{ex} of Eq. (17) become increasingly poorer approximations to the actual numerical values of p_{ex} at these lower pressures. Even for the lowest fractional value (0.04) of Z appearing, the value of p_{ex} corresponding to the limit line for $Z = 0$ is a better approximation to the true value than is that given by Eq. (17). This behavior obviously arises from the fact that the factor $p^{-2/5}$ present in the correction term $Z^{2/3} (\rho_1/p)^{2/5}$ in the square brackets of Eq. (17) causes it to overestimate considerably the Coulomb correction at low pressures where $p < P(Z)$. As a consequence, the truncated series in the square brackets of Eq. (17) yields a reasonable approximation at low pressure only in the mathematical cases of Z close to zero (for $Z << 0.04$, at least). Hence, for the range of low pressures corresponding to Fig. 3, the asymptotic expression of Eq. (19) for the limit

$Z \to 0$ yields a more useful approximation than does p_{ex} of Eq. (17) over the practical range $Z \geq 1$ starting with hydrogen.

One notes that the asymptotic expression of Eq. (20) derived from the results of Rijnierse contains the further negative correction term $Z^{4/3} \ (\wp_2/p)^{3/5}$ within the square brackets, as compared to Eq. (17). Hence, the corresponding value of p_{ex} leads to a further overestimate of the true Thomas-Fermi-Dirac pressure. However, it can be shown that this trend is reversed by inclusion of the next correction term (not discussed in this work) from the results of Rijnierse, which would have the effect of adding a positive quantity to p_{ex} of Eq. (20). The necessity of such behavior was pointed out by Gilvarry in his initial discussion.

It is clear that entirely similar statements can be made on the corresponding range of validity of the asymptotic expressions for the energy, the compressibility, and the thermodynamic parameters associated with the energy and the equation of state, as obtained.

V. DISCUSSION AND CONCLUSIONS

It is obvious that the extended asymptotic relation between the pressures on the Thomas-Fermi-Dirac and Thomas-Fermi atom models as obtained here is a direct consequence of the Thomas-Fermi-Dirac equation but has only a limited usefulness at low atomic number and low pressure. This circumstance is a result of the fact that the first (or first few) terms of an asymptotic series in Z for low atomic number in this case can yield a useful approximation for the limit of low atomic

number simultaneously with the limit of low pressure only if a fairly large number of terms is included from the results of Rijnierse. Note that this stricture does not apply to the expression obtained in I of this series for the limit of vanishing atomic number, because this result is exact (the atomic number Z does not appear in it).

On the other hand, the asymptotic relation obtained between the pressures on the two models has an obvious use at higher pressures, since it specifies precisely how the pressure with exchange approaches the value of the limit line as the pressure increases for fixed atomic number. In this physical case, a single correction term corresponding to the effect of the Coulomb energy reproduces the results from direct solution of the Thomas-Fermi-Dirac equation provided the pressure in question exceeds some limit dependent on atomic number, specified by P(Z) in the foregoing.

The ultimate objective of this series of papers is to construct an asymptotic relation between the pressures on the Thomas-Fermi-Dirac and the Thomas-Fermi atom models which is valid for arbitrary atomic number and, to as great an extent possible, for arbitrary as well as high pressure. The results of this paper impose obvious constraints on the final solution of this problem.

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APPENDIX

In a recent paper, Rijnierse[5] has solved the Thomas-Fermi-Dirac equation by a method of successive integrations and shown that the solution ψ can be obtained to any desired order for the case of small atom radius. Consequently, the Thomas-Fermi-Dirac pressure can be determined to any order, and Rijnierse has evaluated p_{ex} to $p_0 0\,(x_b^5)$. The expression of Rijnierse for the pressure is

$$p_{ex} = p_0 \left[1 - 3^{1/3} x_b/4 - 5\epsilon x_b/4\cdot 3^{1/3} - R_1 x_b^3 + R_2 x_b^3 \ln (4\cdot 3^{2/3}/x_b) + R_3 \epsilon x_b^3\right] \qquad \text{(A1)}$$

in terms of the constants

$$R_1 = \frac{54{,}929}{907{,}200}\,,\quad R_2 = \frac{31{,}500}{907{,}200}\,,\quad R_3 = 3^{1/3}\,\frac{38{,}880}{907{,}200}\,. \qquad \text{(A2a, b, c)}$$

In analogy with the Thomas-Fermi-Dirac pressure p_{ex} of Eq. (16), the pressure p_{ex} of Eq. (A1) can be expressed as a function of the corresponding Thomas-Fermi pressure p_R given by

$$p_R = p_0 \left[1 - 3^{1/3} x_b/4 - R_1 x_b^3 + R_2 x_b^3 \ln (4\cdot 3^{2/3}/x_b)\right]\,, \qquad \text{(A3)}$$

determined from Eq. (A1) by setting ϵ to zero. By making p_R a factor of Eq. (A1) and adding and subtracting appropriate terms, one obtains

$$p_{ex} = p_R \left[1 - (5\epsilon x_b/4\cdot 3^{1/3})\ (1 + 3^{1/3}\, x_b/20 + 3^{5/3}\, x_b^2/400)\right.$$

$$\left. - (\epsilon x_b^2/4)\ (1 + 3^{1/3}\, x_b/10) - (7\cdot 3^{1/3}/160 - R_3)\ \epsilon x_b^3\right], \qquad \text{(A4)}$$

retaining only terms of significant order of approximation. This expression enables one to write p_{ex} as a function of p_R by

$$p_{ex} = p_R \left[1 - (\wp_0/p_R)^{1/5} - Z^{2/3}\,(\wp_1/p_R)^{2/5} - Z^{4/3}\,(\wp_2/p_R)^{3/5}\right] \qquad \text{(A5)}$$

in terms of the constant pressure $\wp_2$ of Eq. (21) in the text and the constant pressures $\wp_0$ and $\wp_1$ previously defined.

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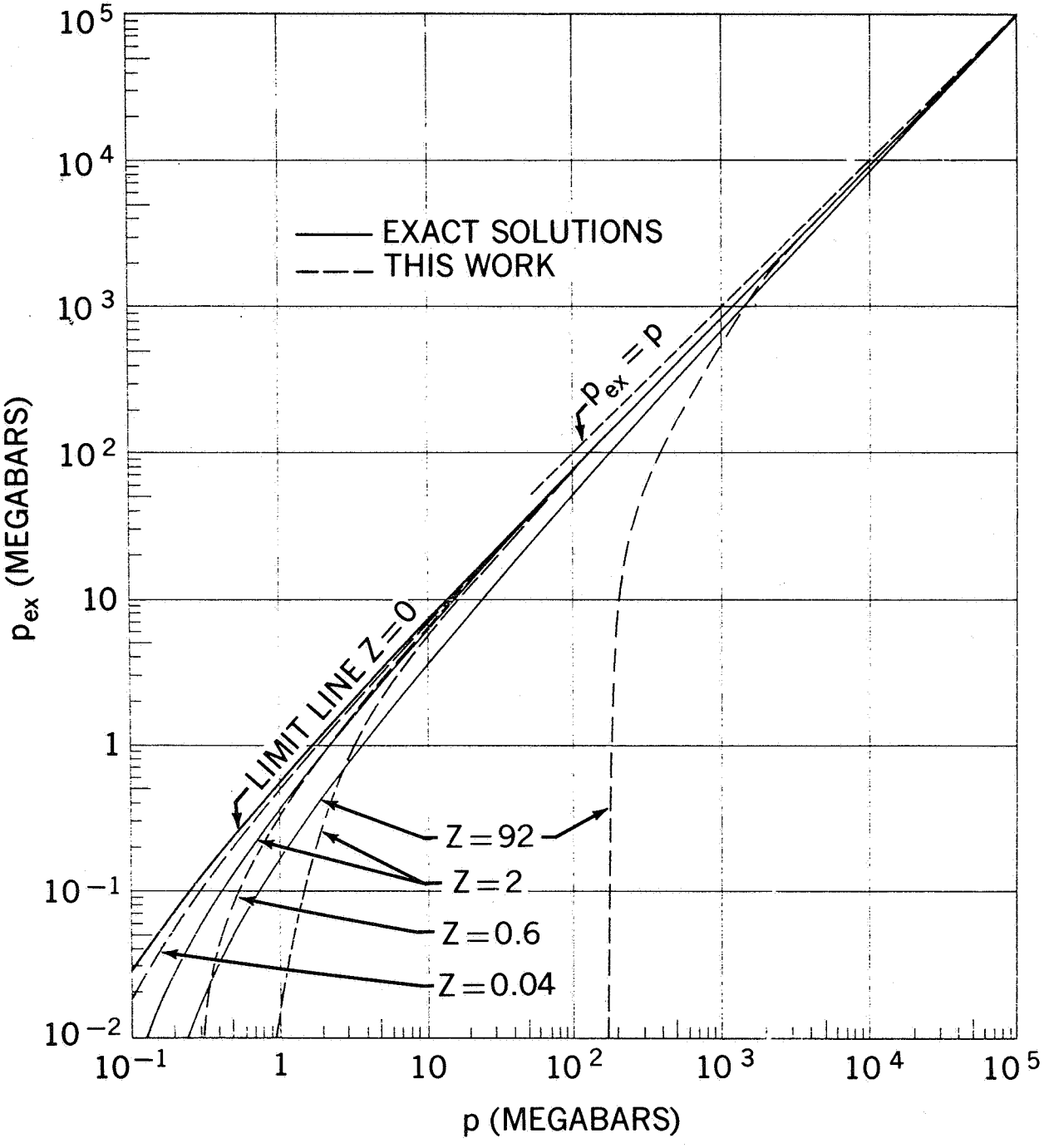
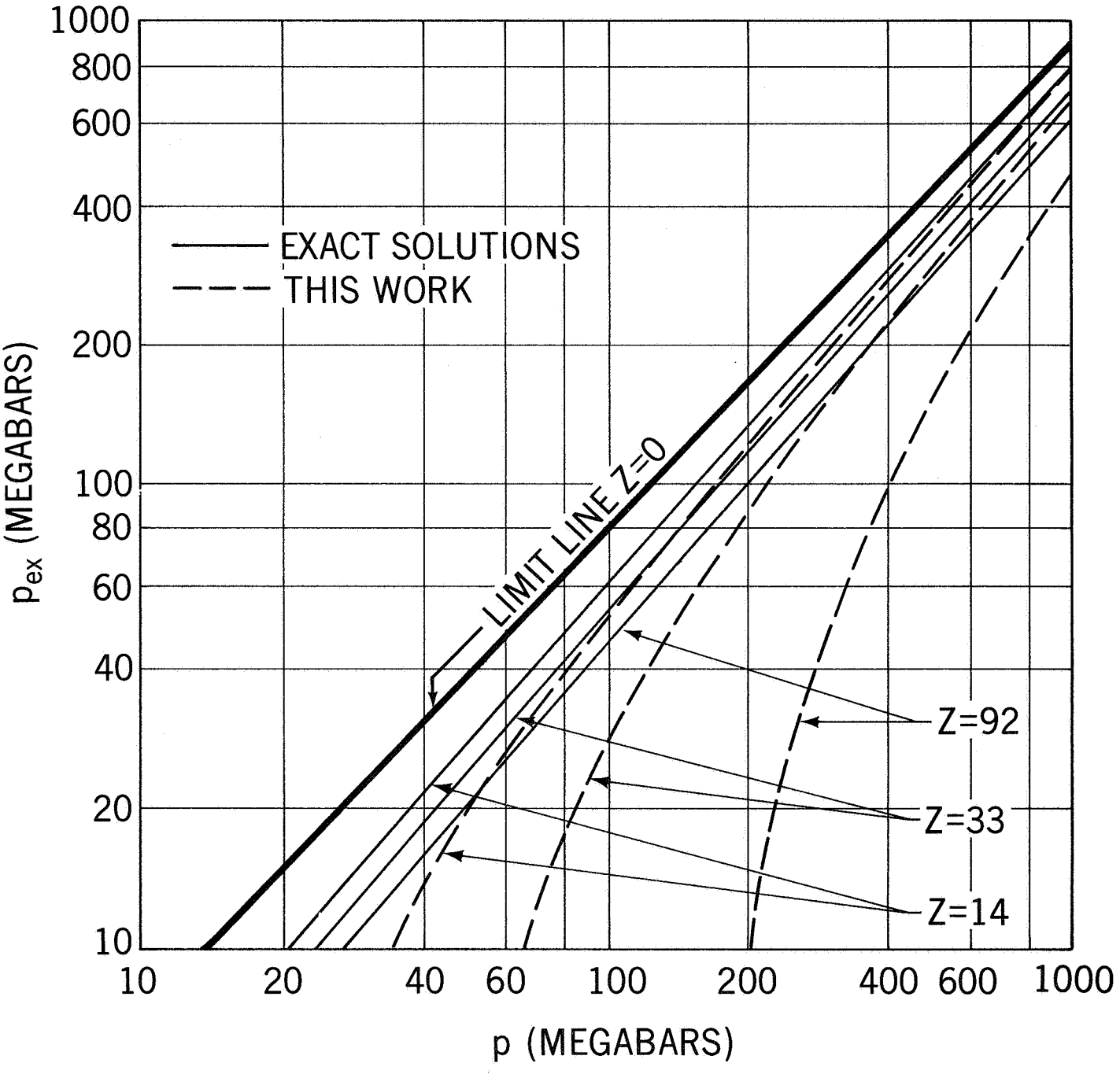
FIGURE CAPTIONS

Fig. 1. Curves of the pressure p_{ex} with exchange as a function of the Thomas-Fermi pressure p for selected values of atomic number Z. The limit line corresponds to Eq. (19) while the remaining solid curves correspond to numerical solutions. For comparison, the dashed curves correspond to the asymptotic expression of Eq. (17).

Fig. 2. Curves of the pressure p_{ex} with exchange as a function of the Thomas-Fermi pressure p for selected values of atomic number Z. The limit line corresponds to Eq. (19) while the remaining solid curves correspond to numerical solutions. For comparison, the dashed curves correspond to the asymptotic expression of Eq. (17). The scales correspond to the intermediate decades of p_{ex} and p in Fig. 1.

Fig. 3. Curves of the pressure p_{ex} with exchange as a function of the Thomas-Fermi pressure p for selected values of atomic number Z. The limit line corresponds to Eq. (19) while the remaining solid curves correspond to numerical solutions. For comparison, the dashed curves correspond to the asymptotic expression of Eq. (17). The scales correspond to the lowest decades of p_{ex} and p in Fig. 1.


EXACT SOLUTIONS
THIS WORK
$p_{ex} = p$
LIMIT LINE Z=0
Z=92
Z=2
Z=0.6
Z=0.04
p_{ex} (MEGABARS)
p (MEGABARS)
10^5
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-1}
1
10
10^2
10^3
10^4
10^5


1000
800
600
400
200
100
80
60
40
20
10
EXACT SOLUTIONS
THIS WORK
LIMIT LINE Z=0
Z=92
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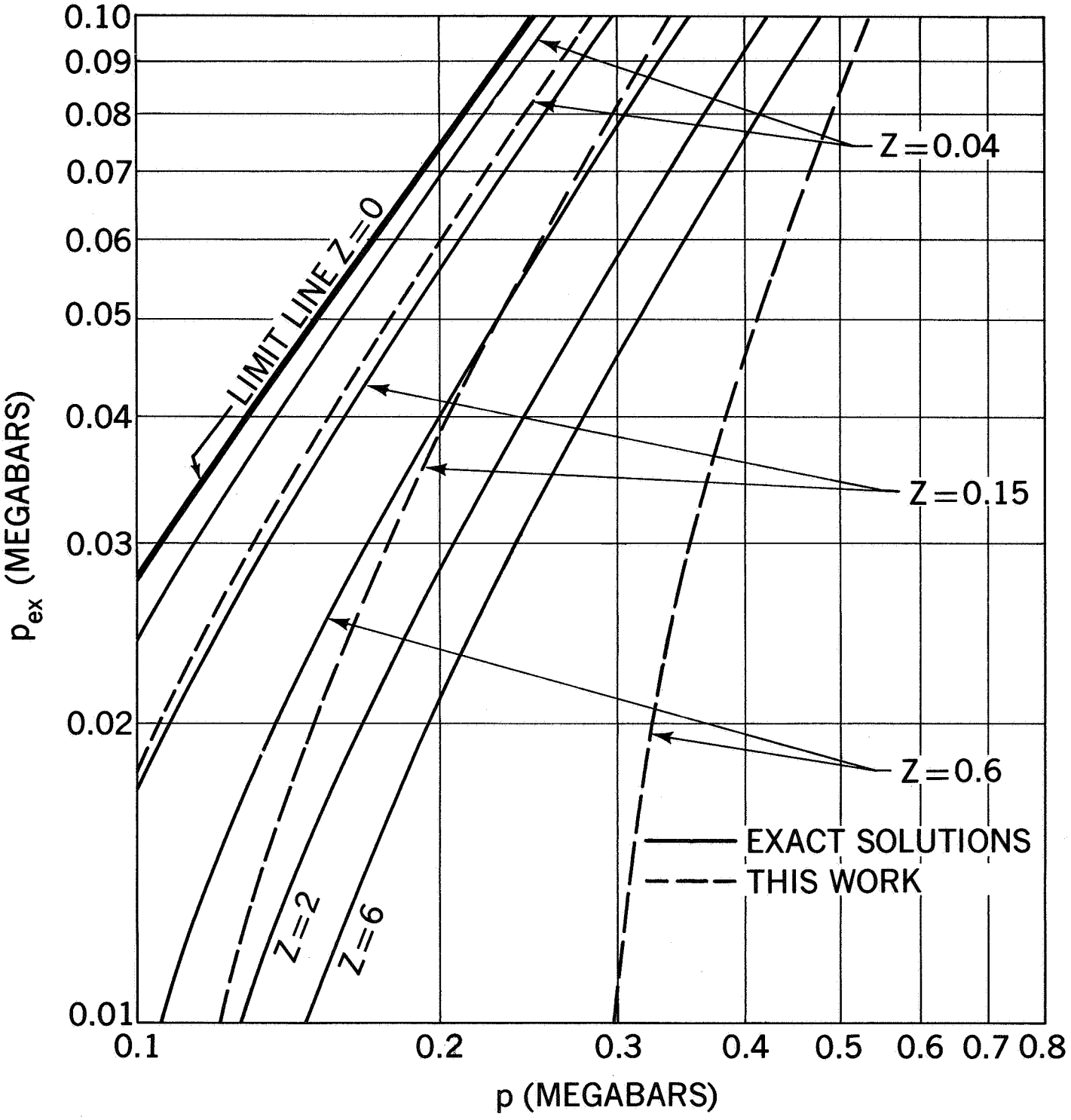
p_{ex} (MEGABARS)
10
20
40
60
100
200
400
600
1000
p (MEGABARS)


0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
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p_{ex} (MEGABARS)
LIMIT LINE Z=0
Z=0.04
Z=0.15
Z=0.6
Z=2
Z=6
EXACT SOLUTIONS
THIS WORK
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
p (MEGABARS)